

LOW-ENERGY SCATTERING OF ELECTRONS AND POSITRONS IN LIQUIDS

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ABSTRACT

The scattering of low-energy electrons and positrons is described for the liquid phase and compared and contrasted with that for the gas phase. Similarities as well as differences are noted. The loci of scattering sites, called "spurs" in the liquid phase, are considered in detail. In particular, their temporal and spatial evolution is considered from the point of view of scattering. Two emphases are made: one upon the stochastic calculation of the distribution of distances required for slowing down to thermal velocities, and the other upon the calculation of cross sections for energy loss by means of quantum mechanics. In these we follow early work by Mozumder and Magee, and by Lekner, respectively.

INTRODUCTION

A fast electron or positron passing through a liquid is known to deposit its energy piecewise, in a large number of discrete locations. Thus the concept of free flight between collisions, which arises so naturally when studying the motions of electrons and positrons in gases, also occurs in liquids despite the great difference in the physical nature of the two scattering milieus, and provides us with an interesting stage for comparison of the two situations. There are similarities as well as differences.

Perhaps the most obvious difference is that the structure of liquids is far more complicated, and correspondingly less well understood, than that of gases. It is only in the past decade that experimental and theoretical results have converged for low incident energy in the case of positron scattering in gases. Therefore we should not expect to understand positron scattering in liquids at a comparable level. For example, we do not know how to calculate cross sections for energy loss at the lowest incident energies for liquids, even for electrons. For gases, the processes responsible for energy loss at lowest energy are simple elastic scattering and (molecules only) rotational excitation for which many high quality calculations and experiments have been performed. In liquids, the lowest energy process is the transfer of kinetic energy from the primary particle into intermolecular vibrational modes of the liquid (i.e., librational excitation, or phonon creation), which is thought to be much more efficient than either elastic scattering or rotational excitation. In any case, the latter is hindered in liquids.

Ionization in the Liquid Phase

For both liquids and gases, most of the energy deposited by the primary particle goes into ionization, electronic excitation, and fragmentation of the absorbing entities. For gases this entity is just one molecule, but for liquids several are normally involved. In either case, secondary electrons are produced. Multiple ionization of a single molecule is much less likely than single ionization, so for the gas phase usually only one secondary electron is produced per collision, but for liquids, several are produced. This is a consequence of the uncertainty principle (see below).

Ionization in the gas phase is a well defined event, and it possesses a definite threshold which can be measured with great accuracy. In liquids, however, there are several effects not present in gases; some of these contribute to a reduction in clarity of the concept of ionization. Besides the production of more than one secondary electron in a typical ionization event, these effects include: (1) The ionized electron enters an energy-absorbing medium upon leaving its molecule; therefore the work required to remove the electron to infinity at rest includes not only the Coulomb energy of

attraction for its parent ion, but also the energy transmitted to the medium in transit. The process responsible for this transfer is stochastic and hence is different for each electron. (2) Many media, especially polar media, trap the ionized electron while it is still in its outbound trajectory. These traps (which can be naturally occurring voids, voids of solvation, or chemical species which bind a primary particle with or without dissociation, etc.) can, in principle, be anywhere in a given medium. (3) All condensed media have dielectric constants greater than unity, which thus reduces the ionization potential compared to the gas phase. Finally, (4) the electron need not be removed to infinity but only to that critical distance r_c where its Coulomb attraction to its parent molecular cation, $e^2/\epsilon r_c$, is equal to the thermal background kT . At this separation, $e^2/\epsilon kT$, the attraction of the electron for its parent ion is indistinguishable from the thermal background. The distance r_c , called the Onsager radius, amounts to about 300 Å for typical organic liquids at room temperature.

Very few secondary electrons actually escape over this thermal horizon. Most have the opposite history, namely, immediate recombination with a molecular cation. This can be understood qualitatively with the aid of the uncertainty principle. Suppose the primary electron deposits 100 eV in a collision. This is typical. The time required for this to happen must be at least 3×10^{-18} sec, by which time the primary particle travels about 10 Å. This establishes the minimum size of the collision region, and gives a rough lower limit on the number of molecules ionized: $10^{-7} \text{ cm}^3 / (M/\rho A)^{1/3}$, where M is the molecular weight of the medium molecules, ρ the density of the medium, and A is Avogadro's number. For hexane this smallest number of molecules is about two. Actually, it is known independently that above five ionizations are produced in n-hexane for each 100 eV of energy loss by the primary particle; or each secondary electron possesses an average energy of 20 eV initially. They are moving much less rapidly than the primary particle, which we can ignore as a consequence, and much more rapidly than the massive molecular cations. Each of the five outgoing secondary electrons therefore looks back on a small entity carrying a total charge of (typically) +5. The slowest of the five electrons immediately falls back into this vast Coulomb hole. The second slowest then sees a charge of +4 and also falls back. And so the process continues until (usually) only one secondary electron is still uncombined. It is interesting that this sequence of recombination proceeds with memory: the electrons recombine geminately; i.e., each with its own parent ion. This is known from the observed scarcity of triplet products.

Focus of this Article

This complicated scenario leads us to a simplification: We need consider only the one surviving secondary electron. The average initial energy of the original five is 20 eV, and the last survivor is the most energetic of the five, so perhaps its energy is 40 eV. If the initial energy of the primary particle is 200 keV and the average energy per deposition is 100 eV (both typical quantities), it follows that for each primary particle there are about two thousand of these surviving secondary electrons, each residing in its own discrete region. These regions or entities are strung out randomly along the trajectory of the secondary particle, and the whole object is called a "track." In a given experiment there may be millions or more of these tracks, one for each primary particle, so the number of entities is billions or more.

Radiation chemists study this microensemble of entities and calculate and measure quantities which represent averages over the microensembles. For positron chemists, the primary particle is the positron itself, and there is no other positron present, so all the attention is given to the very last entity in the track of each primary particle. This entity is unique in the microensemble because it contains the only positron in the system, and because the primary particle forms it at the end of its track when it is slowest. Hence it cannot be argued that it is a typical entity. It is highly arguable that it even resembles a typical entity. The question arises: why do positron chemists study the microensemble? Because if we understand the microensemble (more to the point, a typical entity in the microensemble), then we have a chance of understanding the terminal positron entity. If we don't understand the microensemble as a whole, then we cannot understand the last entity in it.

In this article, we focus our attention on this microensemble of secondary electrons, and

consider their final degradation, starting from a distribution which has a maximum in the neighborhood of 40 eV, and continuing down to thermal equilibrium.

At 40 eV the dominant mechanism for slowing down is ionization and electronic excitation of medium molecules. These dominate other processes down to the threshold for excitation, typically 5 eV. This segment of the degradation process is regarded as being reasonably well understood on the basis of established electronic stopping power laws which yield both the time required and distance travelled by the slowing secondary electron. From 5 eV down to about 0.5 eV, intramolecular vibrational excitation is thought to provide the most important slowing down mechanism. This also is fairly well understood, from the viewpoints of both calculating and measuring cross sections and of computing ranges and times in the segment. Below 0.5 eV down to kT, the story is quite different: although it is believed that we have identified the degradation processes (excitation of intermolecular vibrations), we do not know how to calculate cross sections for them. Times and distances in this last segment are less certain, but can be inferred from sweeping electric field measurements and from microwave conductivity measurements.

In the remainder of this article, we consider mainly this last segment, which has been called the subvibrational region, from two viewpoints: Purely phenomenological descriptions of the degradation process using assumed cross sections, and considerations of ways to determine the cross sections themselves from first-principles quantal calculations.

PHENOMENOLOGICAL DESCRIPTION OF THERMALIZATION

The calculation of track structure of the primary particle has recently become an active area of research. The ever decreasing cost of computation has made large scale Monte Carlo calculations feasible. These calculations use cross sections from experiment and from other calculations. Calculations of the spatial, temporal, and ergodic development of the entities along the tracks are not as numerous or successful because the required cross sections are not all known, as we have already pointed out. However, the qualitative nature of the physical and chemical processes operating in the developing entities is fairly well known. It is inviting to conduct model calculations based on the known qualitative features, using assumed cross sections, and to try to reproduce relevant experimental observations.

The development of entities can be divided into two parts which we call the prethermal or physical regime and the postthermal or chemical regime. At the end of the prethermal regime, the secondary electron becomes thermalized. This takes one to ten picoseconds. In the postthermal regime, the secondary electron moves around by diffusion and engages in chemical reactions. This region terminates by recombination or some other reaction, and is essentially complete in a microsecond. Even though the boundary between these two regions is not perfectly distinct, the two-region concept is nevertheless useful.

We have already discussed three subregions or segments of the prethermal regime: ionization and electronic excitation (40 to 5 eV), intramolecular vibrational excitation (5 to 0.5 eV), and intermolecular vibrational excitation (0.5 to kT). At this point the secondary electrons in the microensemble are thermalized and have established a distribution f of thermalization distances r_{th} (as measured from the cation). The functional form of $f(r_{th})$ is important and can be inferred from sweeping field measurements, but there is a good deal of uncertainty and controversy regarding its shape. [1,2] It is this function which provides the point of contact between theory (calculations of the prethermal regime) and experiment. We now describe this connection.

If an electron comes to rest a distance r_{th} from its parent cation, it is attracted to it by the Coulomb potential $V(r_{th})$. The probability that it will diffuse away, beyond the Onsager radius r_c , is given by a Boltzmann factor:

$$g(r_{th}) = \exp(-V(r_{th})/kT) = \exp(-r_c/r_{th}) \quad (1)$$

This result is not at all obvious but rather is a seminal contribution by Onsager, [3] who demonstrated that $g(r)$ is the long time solution of the Smoluchowski equation which describes diffusion of a particle in a Coulomb field. It follows from eq. (1) and the physical meaning of the distribution function f that P_{calc} , the calculated probability for the whole microensemble for diffusion of secondary electrons out of the entity and into the bulk liquid, is given by

$$P_{calc} = \int f(\vec{r}) g(r) d\vec{r}. \quad (2)$$

This quantity can be measured and is tabulated for many liquids. [4,5] It is the ratio of the yield of free electrons in the bulk of the liquid (ie., beyond the Onsager radius) in the absence of an external field to the limit yield for high electric fields. Its value depends upon temperature, solute concentration, etc., and the correlation of the calculated and the measured value for various trial distribution functions f constitutes the connection between theory and experiment, and tells us what we know about the functional form of f .

Historically, much more attention has been paid to the postthermal regime. Starting from thermalization, one calculates subsequent development of the entity by solving a diffusion equation using $f(\vec{r}_{th})$ as the distribution of secondary electrons at $t = 0$. Thus $f(\vec{r}_{th})$ has come to be known as the "initial" distribution, even though it describes where the electrons are at the conclusion of the prethermal regime.

We now turn to the calculation of the initial distribution function $f(\vec{r})$ and the theoretical deduction of the escape probability for the microensemble, P_{calc} . A procedure for the calculation of f was given a long time ago by Mozumder and Magee. [6] Some other workers have attempted to calculate f also, [7-11] but we like the prescription of Mozumder and Magee because it is instructive, it replicates well the actual physical events, and is easy to understand. It requires considerable calculations, however, and has not yet been put to an exhaustive numerical test to our knowledge.

First one chooses ΔE , the initial energy of the secondary electron. This determines R_v , the distance travelled in the first two segments of the prethermal regime, that is, from an energy of ΔE down to E_v , the threshold of the subvibrational segment. (See fig. 1.) For $\Delta E = 40$ eV and $E_v = 0.5$ eV (our example values), this distance is known to be about 25 Å for most nonpolar liquids. From that point to thermalization one assumes the secondary electron proceeds by a random walk. The number of steps N in the random walk can be deduced in terms of p , the probability of exciting an intermolecular vibrational mode in a given mean free path (which are mostly for elastic scattering), and ω_v , the vibrational quantum lost per inelastic collision, by an energy balance argument: At the point R_v , the energy of the particle is $E_v - e^2/\epsilon R_v$; after thermalization it has travelled to a new point R_T from the cation and has lost the energy $Np\omega$ to the medium. Hence

$$E_v - \frac{e^2}{\epsilon R_v} = \frac{3}{2}kT - \frac{e^2}{\epsilon R_T} + Np\omega. \quad (3)$$

By assuming a value for the product $p\omega$, one can calculate N for any given R_T . R_T is fixed by the variables of integration in eq. (2): We choose r and θ , the coordinates of the point of thermalization measured from R_v (see fig. 1). The law of cosines give R_T , and eq. (3) gives N . Clearly the bulk of the work lies in calculating $p\omega$, for therein lies the cross section for intermolecular vibrational excitation. This quantity, which depends upon the energy of the incident secondary electron, is to be gotten from a quantum mechanical calculation, but we do not know how to carry it out. By trial and error, Mozumder and Magee arrived at a value of 5.5×10^{-4} eV per collision, elastic or inelastic. [6] Using this value along with $\Delta E = 40$ eV, $E_v = 0.5$ eV, $R_v = 25$ Å, $T = 298$ K, and $\epsilon = 1.9$, we find N to be 460 for $R_T = 80$ Å (a representative value of the thermalization distance for nonpolar liquids). Such a large number of steps suggests that a Gaussian distribution is accurate:

$$f(\vec{r}) = \left(\frac{1}{2 \pi N L^2} \right)^{3/2} \exp(-3r^2/2NL^2). \quad (4)$$

L is the mean free path for elastic collisions. Mozumder and Magee somewhat arbitrarily take it to be the mean molecular separation of molecules in the liquid. Equation (4) is slightly misleading, for N depends upon R_T and hence on r and θ , and the N -dependence of the preexponential factor must be included in the integrand in eq. (3). Another consequence of the R_T -dependence of N is that f as written above is not normalized; one must divide the right hand side of eq. (2) by $\int f d\vec{r}$.

The integration in eq. (2) is performed numerically and yields the escape probability of all entities with $\Delta E = 40$ eV. However, there is a distribution of ΔE values for a given value of E , [12] the energy of the primary particle when it enters the medium. This distribution is known, more or less. There is also a distribution of E values, and this depends on the nature of the source of primary particles. P_{calc} depends upon ΔE and must be averaged over it with the appropriate distribution function. The whole numerical process is shown schematically in fig. 2. The result of all this work will be the yield of bulk secondary electrons appropriate for the experiment.

This procedure amounts to a poor man's Monte Carlo calculation. There are a number of approximations: The use of a Gaussian (eq. (4)) implies we are ignoring the Coulomb influence of the cation during the random walk. The parameters L and p_0 clearly should depend on the energy of the secondary electron; the dividing line between the segments of the prethermal regime are not as sharp as we have portrayed; the procedure as prescribed above is limited to one electron-cation pair per entity; and it ignores trapping by density fluctuations and scavenger solutes. Perhaps more significant is that time is not a part of the procedure, as it must be in order to include the influence of an externally applied electric field. The latter extension can be made, either with an after-the-fact modification of the procedure just described, or by integrating the Fokker-Planck equation in some appropriate approximation. [13]

New data indicates that straight chain saturated hydrocarbons are very effective traps for positrons with energies near 0.3 eV. [14] The mechanism is apparently the formation of vibrational resonances. For hexane, the cross section for this is quite considerable, about 1.5 \AA^2 , which corresponds to a mean free path of about 140 \AA . A random walk of 460 steps, each 5 \AA , will almost always be terminated by capture into such a resonance, and this result must be accommodated in an application of this procedure to positron thermalization for such liquids.

CALCULATION OF THE CROSS SECTIONS FOR SCATTERING IN LIQUIDS

The process under consideration in this section, the excitation of intermolecular vibrational modes, is difficult to study experimentally, because the energy quanta involved, about 0.001 eV, are in the far infrared. The Raman shift is observable for many liquids, and gives us the best information we have for the process. In principle, a knowledge of the oscillator strength distribution yields the cross section. Thermal diffusion data also yields some information, the idea being that energies of the subvibrational region are so low that the processes for energy loss (and gain) must be similar to those operating in the postthermal regime. Thus the mobility or the diffusion constant, or, equivalently, the momentum relaxation time for free Brownian motion, become crucial quantities.

Rather than proceed in this direction, we consider another system, closer to the interests and expertise of most of the conferees: argon. Liquid argon is at once simpler and more complicated than liquid hexane. Atoms are much simpler to treat quantum mechanically than molecules, but the absence of intermolecular vibrations eliminates one of the segments from the prethermal regime, and cooling below the threshold for electronic excitation relies on intermolecular vibrational excitation and on elastic scattering from atoms and from density fluctuations. These are inefficient cooling mechanisms, and the cooling electron has so much energy in the bulk of the segment where they are operating that the random walk assumption which fueled our phenomenological discussion above

is not valid.

In the remainder of this concluding section we consider the influence of the liquid medium on the calculation of elastic scattering cross sections for atomic argon. Specifically, we want to know what polarization potential to put into the scattering equation (using atomic units now and in the remainder),

$$(-1/2 \nabla^2 + V_{\text{stat}} + V_{\text{pol}} - 1/2 k^2) \psi(\vec{r}) = 0 \quad (5)$$

where V_{stat} is the static potential provided the incident electron or positron by the nucleus and the target electrons, and V_{pol} is the polarization potential. The latter has the well known form $-\alpha/2r^4$ for an isolated atomic target at long range. At short range it is customary to multiply this by a function $w(r)$, commonly known as the cut-off function, which moderates the strongly diverging short range behavior and hopefully includes some of the effects of short range correlation. For the liquid phase, we know that the polarization potential is screened at long range by the intervening atoms. We follow the important work of Lekner [15] in describing the calculation of this screening. The experimental quantity for comparison is the drift velocity of electrons in the liquid as a function of electric field strength. The comparison requires cross sections for elastic scattering and for momentum transfer.

Consider fig. 3, which is taken from ref. [15]. The polarization potential experienced by the atom at \vec{R} due to the electron has the direct contribution $-\alpha w(r)/2r^4$ and the indirect contribution due to the induced dipoles in all the atoms, one of which is shown at \vec{t} . Lekner defines a function $h(R)$ so that the total field at \vec{R} is

$$\frac{1}{R^3} h(R) \vec{R} \quad (6)$$

This has the direct part $1/R^2$ and an indirect part. To deduce the latter, consider the field at \vec{R} due to a dipole $\vec{\mu}$ at \vec{t} :

$$\vec{E}(\vec{s}) = \frac{3 \vec{s} (\vec{\mu} \cdot \vec{s}) - s^2 \vec{\mu}}{s^5} \quad (7)$$

We must sum this field over all atoms except the one at \vec{R} , but in doing so we may take advantage of the fact that the result will be in the direction of \vec{R} , so we need only include the component of $\vec{E}(\vec{R})$ along \vec{R} in the average:

$$\frac{1}{R^3} h(R) \vec{R} = \frac{1}{R^3} \vec{R} - \frac{\vec{R}}{R^3} \int n_{\text{pr}}(s) \vec{R} \cdot \vec{E}(\vec{s}) d\vec{s} \quad (8)$$

The sum over atoms is accomplished by use of $g_{\text{pr}}(s)$, the pair-correlation function of the liquid, and n , the average number density of the atoms. The dipole $\vec{\mu}$ is clearly

$$\vec{\mu} = \frac{\alpha}{t^3} h(t) \vec{t} \quad (9)$$

which displays the essential role of self-consistency in the determination of the function h by solving the integral equation (8). The pair-correlation function is known, and straightforward iteration leads one directly to a realization of h .

The potential seen by the electron due to the polarization, direct and indirect, of the atom at

R is evidently

$$-\alpha w(r) h(r)/r^4. \quad (10)$$

Unfortunately this result cannot be used to calculate phase shifts by using it as V_{pol} in eq. (5), because the scattering electron (or positron) is never interacting with one atom across free space, but rather is always interacting with intervening atoms as well. Lekner responds to this quandary with the following construction: First we average $V_{\text{tot}} = V_{\text{stat}} + V_{\text{pol}}$ (the latter being given by eq. (10)) over the ensemble:

$$\langle V_{\text{tot}}(r) \rangle = V_{\text{tot}}(r) + \int n g_{\text{pr}}(s) V_{\text{tot}}(s) d\vec{s} \quad (11)$$

Now, since the scattering particle responds only to changes in the potential and not to its magnitude, we can subtract off a constant value and truncate. Lekner defines the effective scattering potential to be

$$V_{\text{eff}}(r) = \langle V_{\text{tot}}(r) \rangle - \langle V_{\text{tot}}(r_0) \rangle \quad \text{for } r < r_0 \quad (12)$$

and zero beyond, where r_0 is the location of the first maximum in $\langle V_{\text{tot}}(r) \rangle$. The calculated cross section for the liquid and gas are compared in fig. 4, and the comparison between theory and experiment for the drift velocity is shown in fig. 5.

The limited question of how the gas phase polarization potential should be modified in order to accomodate scattering in liquids has been addressed. The approximations made are that fluctuations in the number density do not effect the scattering process, and that multiple scattering effects are negligible. The former approximation has been called into question by Basak and Cohen, [16] who believe that the scattering of thermal electrons in liquid argon is dominated by a deformation potential produced by long-wavelength density fluctuations.

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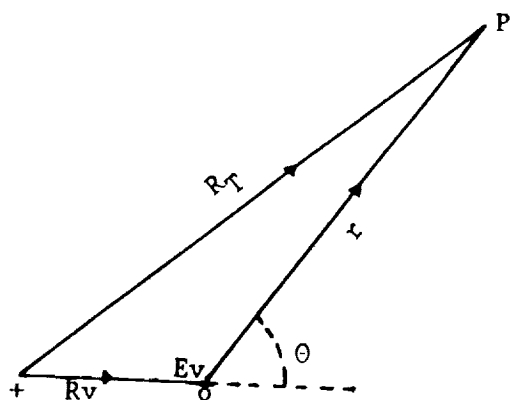


Fig.1. The coordinates involved in the random walk calculation

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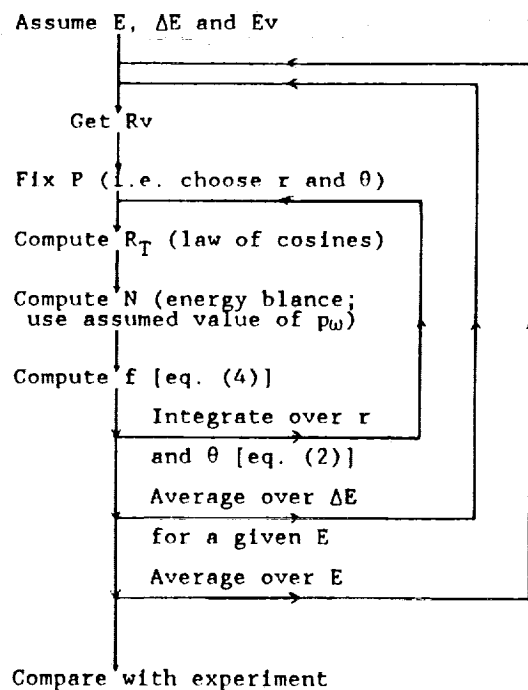


Fig.2. Schematic of the calculation of the field of bulk secondary electrons.

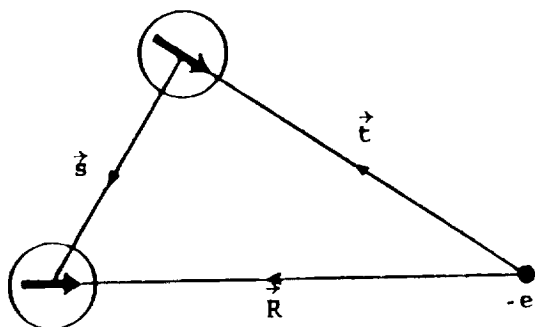


Fig.3. Local fields in liquids. The field on the atom at R is the sum of the direct field plus the dipole fields of atoms at all other points t.

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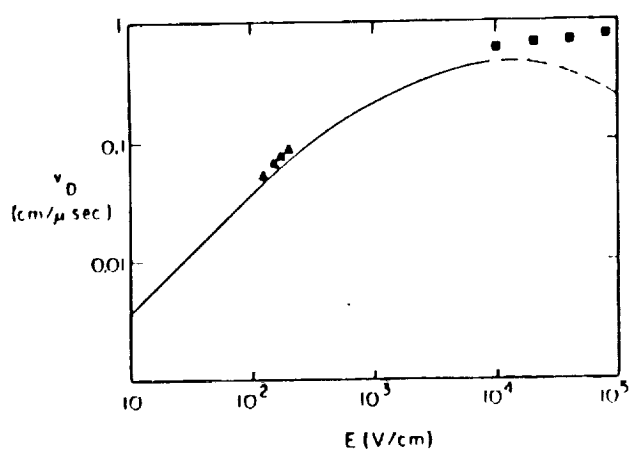


Fig.5. Calculated drift velocity in liquid argon (line) compared with experiment. Cross sections at high field are not accurate.

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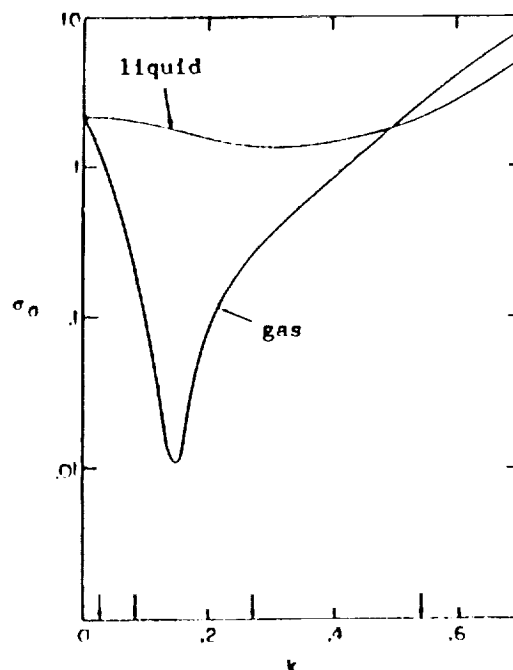


Fig.4. Elastic cross section σ_0 (in units of $4\pi a_0^2$) calculated for the gas and liquid as functions of momentum k (in units of a_0^{-1}).

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